EFFECT OF B_2O_3 GLASS ADDITIVES ON PHYSICAL CHARACTERISTICS AND DIELECTRICS OF BARIUM MAGNESIUM TANTALATE $Ba(Mg_{0.33}Ta_{0.66})O_3$

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Abstract

Barium magnesium tantalate (BMT) was prepared by two step solid state route at different temperatures in the range 950 to 1300^0C by soaking the sample for various time intervals ranging from 2 hrs to 39 hrs. In another set of experiment BMT was added with 1, 2, 2.5, 5, 7.5 and 10 wt% B_2O_3 (frit glass) and heated at 1300^0C for 30 minutes. The samples obtained at the end of thermal history were pelletized and subjected to crystal structural, density, surface morphology and dielectric measurements. XRD studies indicate that single phase BMT pseudo cubic perovskite was formed by heating sample at 1200^0C for 2 hrs. This clearly indicates that reduction in phase formation temperature was observed for pure BMT formed by two step solid state route.

The observed density of pure BMT sample was 4.35 gm/cc which is far below the theoretical density (7.89 gm/cc); hence glass addition was carried out in the range of 1 to 10 wt%. It is observed that highest densification was obtained for sample with 2.5 wt% B_2O_3 (97.36%). The 5 wt% B_2O_3 added sample showed good surface homogeneity and its dielectric measurements studies showed a dielectric constant of 22.5 at the resonance frequency of 6.94 GHz. The BMT samples with 7.5 and 10 wt% B_2O_3 on sintering were found to be mechanically harder however their surface becomes uneven as compared with the pure BMT or with lower (<5wt%) B_2O_3 compositions. All the above samples were heated at or below 1300^0C

Key words: BMT, XRD, dielectric ceramic.

I. Introduction:

$Ba(Mg_{0.33}Ta_{0.66})O_3$ and related materials of the family exhibit perovskite structure or ABO_3 where Ba^{2+} is at A site and B site is shared by Mg^{2+} and Ta^{5+} making the structure of a general stoichiometry $A(B_{1/3}B_{2/3})O_3$. Perovskites are the most widely studied family of materials in microwave ceramics. $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) and $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) are most widely studied materials in this family and are commercially produced for applications like radio antenna, resonators in satellite communications. It has been reported that BMT prepared by various routes shows εr in the range 23 to 25 with τf in the range 0

to 5 (ppm/^{0}C) and Qxf in the range 84,000 to 4,30,000(GHz). The observed wide variation in properties generates from the method of synthesis, sintering temperature additives and dopants. The most popular method is solid state synthesis which requires1650^{0}C for 20 hrs. The resultant pucks show properties as εr- 25, τf -5, Qxf -430000GHz. (430 THz) [13]. Review of extensive work in area of microwave dielectrics has been done and reported by M.T Sebastian [13].

II. Aims and objective:

The major problems associated with bulk manufacture are a) high sintering temperature (1650^{0}C) and b) time (20 hrs.) which increases processing cost; c) high sintering temperature introduces non-homogeneity in material and d) high cost of tantalum oxide (extra pure). In the present work we have tried to addresses these issues by a) reduction in the sintering temperature, b) reduction in sintering time c) systematic study on phase formation of BMT material in the temperature range 950 to 1300^{0}C for 2 hrs using XRD, SEM, Dimensional analysis and densification, d) study of effect of B_2O_3 glass additives in BMT.

III. Experimentation:

a) For synthesis of BMT two step process was adopted. The said process is used by other workers [14, 15, 16] for studying zirconium doping, formation and effect of $Ba_5Ta_4O_{15}$ on dielectric properties of BMT. In the present work we have followed two step method [13] in which $MgTa_2O_6$ binary oxide with tetragonal structure was prepared by solid state route at 1200^{0}C for 2 hrs formation of $MgTa_2O_6$ was confirmed by XRD (JCPDS 32-631). $MgTa_2O_6$ was then added with $BaCO_3$ to give final stoichiometry $Ba(Mg_{1/3}Ta_{2/3})O_3$. The mixture was crushed for 3 hrs and then sieved through 300 micron mesh. The mixture was slowly heated and till 1300^{0}C and kept at final temperature for half an hour. The product was allowed to furnace cool overnight. The sample was in beige colored powder form. The crystal structure was determined using BRUKER AXS D-8 X-ray diffract-o-meter in the range of 2θ = 20-80.

b) After confirmation of $Ba(Mg_{1/3}Ta_{2/3})O_3$ phase formation about 2 gram material was pressed into pellet 15 mm dia. 3mm thickness) and sintered at 1200^{0}C for different time intervals from 2 hrs to 40 hrs. After every sintering cycle XRD measurement were carried out to identify sintering time for single phase formation. (Fig:1) Periodical measurement of density and weight were carried out which indicated that there is no significant densification and theoretical density reached only 57.7%.

c) In another set of experiments B_2O_3 was added in different wt% (1, 2, 2.5, 5, 7.5 and 10) to BMT powder obtained at the end of step 'a' as described earlier. All compositions made this way were compacted (diameter 15 mm and thickness 2-3 mm) using hydraulic pellet press at 5 ton pressure for 1 min. 5%PVA binder was added for compaction. All the pellets were sintered at 1300^{0}C for 30 min. All pellets were furnace cooled and studied using XRD (BRUKER AXS D-8) and SEM (JEOL JSM 6360 A) for studying phase formation and surface morphology, respectively.

d) All compacts made in earlier step were subjected for dimensional analysis, density measurement and color was recorded.

e) Sintered samples were subjected to dielectric measurements by using single cavity for dielectric constant and 'Q'-factor measurement method by using a cavity of dimensions 21mm X 21mm X 17mm. Using Teflon as low loss dielectric. A continuous frequency sweep was taken from 1 to 10 GHz. To verify the practical results obtained, a reverse analysis was performed on full 3-D Electromagnetic (EM) tool HFSS, using the parameters available.

IV. Results and discussion:

BMT formed by conventional one step requires to be sintered at 1650^0C for 20 hrs and it contains $Ba_5Ta_4O_{15}$ as a secondary phase however, the two step method where $MgTa_2O_6$ was prepared first and then incorporated with $BaCO_3$ reduces the sintering temperature and soaking time required to density BMT.

From XRD patterns in fig 1, it is seen that formation of BMT starts at a temperature as low as 950^0C however; it contains some un-reacted Ta_2O_5 and $BaTa_2O_6$. Further heating of the same mixture at 1200^0C for 2 hrs results in the formation of desired perovskite phase as can be seen from 111 reflection 2θ at 38. Further sintering of the same material reduces the secondary phases significantly and finally at calcinations history of 1200^0C, 39hrs and 1300 ^{0}C, 2 hrs it gives single phase BMT.

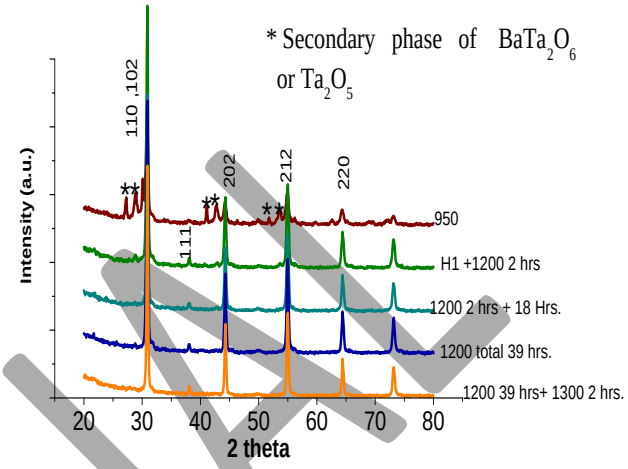

Fig.1 XRD patterns of BMT

TABLE I Densification study of BMT with and without additives

Composition	%wt loss after heating at 1300^{0}C	Axial Shrinkage after heating at 1300^{0}C	Radial Shrinkage after heating at 1300^{0}C	Density in gm/cm^3 after heating at 1300^{0}C Cycle 1	Density in gm/cm^3 after heating at 1300^{0}C Cycle 2	% theoretical density after cycle 1
BMT	1.557	13.88	0	4.38	4.5	57.7
BMT + 1% B_2O_3	1.346	12.30	10.89	6.44	6.32	84.4
BMT + 2% B_2O_3	0.894	12.12	12.53	6.23	5.83	82.2
BMT + 2.5% B_2O_3	0.690	13.49	12.5	7.39	6.55	97.36
BMT + 5% B_2O_3	3.278	No change	16.3	5.96	5.95	78.52
BMT + 7.5% B_2O_3	0.585	No change	4.69	4.23	4.23	55.7
BMT + 10% B_2O_3	0.888	0.77	No Change	3.87	3.53	50.98

After every stage of heating the dimensions and weight measurements of the pellet were noted and shown in Table -1

It was observed that no significant shrinkage is seen in the pure BMT pellets during sintering. At 1300^{0}C sintering history the observed density was 4.38 which is 57% of the theoretical density. Further densification will happen after repeated cycles at 1300^{0}C or higher temperature as can be seen from Table 1.

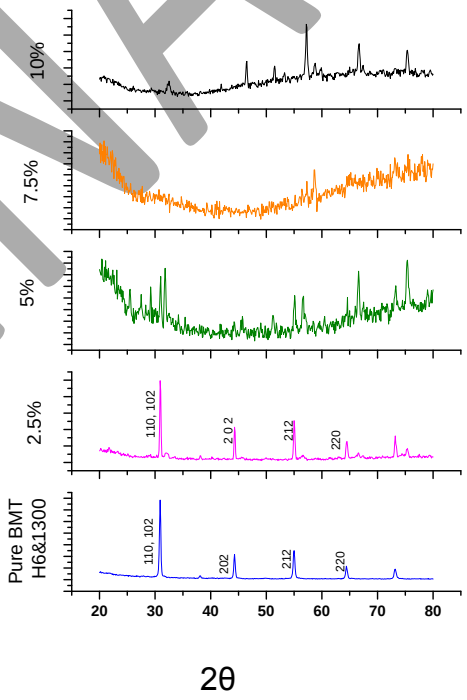

Fig. 2. XRD pattern of BMT with and without B_2O_3

BMT sample prepared by using 2 step method as explained earlier, the mixture of $MgTa_2O_6$ +$BaCO_3$ was heated at 1300^{0}C and soaked for 30 min. To this material B_2O_3 was added in 1, 2, 2.5, 5, 7.5 and 10 weight percent. All these mixtures were crushed for 2 hrs in agate mortar and

added with few drops of 5% PVA solution as binder and compacted. The pellets thus formed showed better homogeneity and higher mechanical strength and smooth shiny surface as compared to pure BMT pellets. On sintering the color transformed to yellow with varying degree of intensity. After every heating cycle measurement of dimensions and weight showed that in B_2O_3 added pellet there is markedly higher shrinkage resulting in to the densification of pellets. It is observed that 2.5% B_2O_3 added pellet reached a highest density 7.39g/cc which is 97% of the theoretical density. It is also observed that as the density increases, pellets became intense yellow. The XRD pattern (Fig 2) indicates that in the higher compositions of B_2O_3 the overall crystallinity is lower than that observed for the pure samples.

It is also observed that for higher compositions (>5wt %) of B_2O_3 compacts are mechanically harder however, its surface becomes uneven as compared to pure BMT or lower compositions (<5wt %) of B_2O_3. The role of glass addition as a binder and connector is best seen through SEM images. BMT without glass show individual grain not fused as can be seen from Fig.3. Addition of 1 wt% B_2O_3 glass results into connectivity of grain producing continuous and homogenous surface. It is seen that on 2% addition of B_2O_3 the connection between neighboring grains give larger sized grains. A very interesting feature is seen in SEM of BMT with 2.5% B_2O_3, There are well developed hexagonal rods of about 10 micron size in length. The population of these hexagonal rods appears throughout the surface and not only at some isolated sites. The hexagonal rod appears translucent suggesting prominent role of B_2O_3 in interconnecting BMT crystallites to give long hexagonal rods. On further addition of B_2O_3 the rod size appears to be decreased to the length of 4 microns. This feature disappears beyond 5% B_2O_3. The exact composition of rod and whether they are hollow or filled will be cleared from TEM studies.

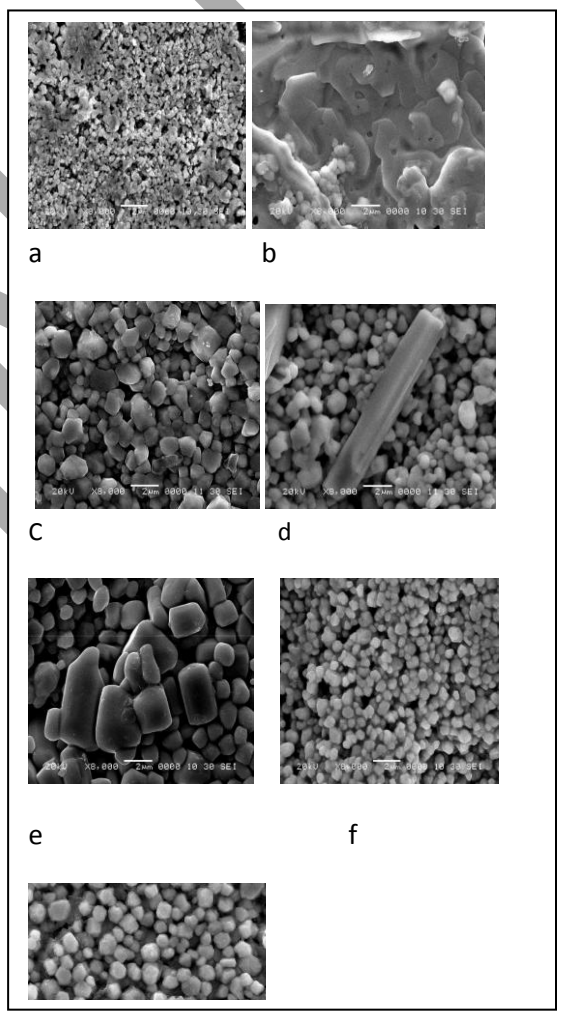

Figure 3. SEM images of Pure $Ba_3(Mg_{1/3}Ta_{2/3})O_3$ and additives from top a) Pure b) 1% c) 2%d) 2.5% e)5% f)7.5% g) 10% B_2O_3.

We carried out dielectric measurements for only 5%B_2O_3+BMT composition since it has

smoothest surface amongst all the synthesized compositions. First resonance was observed at 6.5662 GHz (TE01δ mode) and second resonance was present at 6.9762 GHz (HE mode. The 'Q'-factor observed for TE01δ mode is roughly 338, while that for the HE mode is around 836. Both the modes moved higher when they were perturbed by the metallic plunger from the top, thereby confirming the identity of modes. To verify the practical results obtained, we performed a reverse analysis on full 3-D Electromagnetic (EM). To verify the practical results obtained, we performed a reverse analysis on full 3-D Electromagnetic (EM) tool HFSS, using the parameters available.

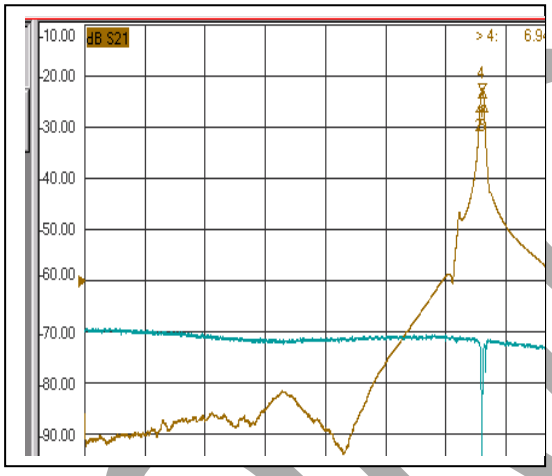

Figure 4. Dielectric measurements on BMT+5% B_2O_3

Wide band sweep from 1 GHz to 10 GHz, showing dominant mode (i.e., 1st mode), TE $_{01\delta}$ and second higher order mode, HE, along all other higher order existing modes. A DR with identical dimensions was placed in the cavity and Eigen mode analysis was carried out. It verified the presence of TE01δ mode and HE mode at the practically obtained frequencies for the dielectric constant values between 21.5 and 22. The EM field patterns were also observed which verified TE01δ mode and HE mode.

V. Conclusions:

The two step method helps in preventing formation of secondary phase $Ba_5Ta_4O_{15}$ during the synthesis of BMT material, hence it is a better method of synthesis as compared to conventional single step state route. At low (1300C) sintering temperature disordered cubic perovskite phase is observed. High temperature (1600C) sintering results in 1:2 ordered hexagonal crystal structure. 2.5 wt% Glass addition in BMT material gives highest densification and gives 97% theoretical density. 5 wt% Glass addition in BMT material gave excellent surface homogeneity and has ε_r = 22.5 at 6.3 GHz

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